PHOTOELECTRIC AND THERMIONIC PROPERTIES OF PALLADIUM

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Abstract

The photoelectric and thermionic properties of pure palladium were studied during an extended outgassing in high vacuum. The *threshold*, obtained by extrapolation of spectral sensitivity curves, shifted from below 2300A to above 3000A and then back to a *final* value of 2486A as outgassing progressed. In the final state the photocurrents excited by monochromatic light *increase with temperature*, the relative increase being greater for the longer wave-lengths. At the higher temperatures the spectral sensitivity curves approach the axis asymptotically. The results are shown to be in excellent agreement with Fowler's recent theory and his method of analysis yields the value 4.97 ± 0.01 volts for the true work function (2486A). The *thermionic work function* for the clean specimen was found to be 4.99 ± 0.04 volts, and the value of the constant A is very close to 60 amp./cm^2 deg^2.

I. Introduction

ALTHOUGH it was only a few years ago that it could be said that there was not a single metal for which the photoelectric threshold for the thoroughly outgassed state was accurately known, there are today no less then 12 metals for which the photoelectric properties have been carefully investigated under modern high vacuum conditions.[1] One is now justified in examining the existing data for general relationships between the photoelectric and other properties of the elements. In particular, it is well known that there is a definite relation between the photoelectric work function and the position of the element in the periodic table, for we find that the metals at the beginning of each period—the alkalis and alkaline earths—have very low work functions and there is a general tendency toward higher values at the end of each period. In 1927 one of the authors[2] reported a study of platinum (the last element in the third long period) in which it was found that its work function when thoroughly outgassed was approximately 6.3 volts, the highest value yet reported for any clean metal. This at once raised the question as to whether the elements palladium and nickel which occupy corresponding positions in the previous periods would also show unusually high work functions when clean. Accordingly the authors undertook a study of palladium, the results of which show that the work function of this metal, while considerably lower than that of platinum, is nevertheless definitely higher than for any other element in its period. A recently reported study by Glasoe[3] shows the

[1] The measurements have been summarized in Chap. III of "Photoelectric Phenomena" by Hughes and DuBridge (McGraw-Hill Book Co., in press). There are only three metals for which *both* the thermionic and photoelectric work functions are accurately known.

[2] L. A. DuBridge, Phys. Rev. **29**, 451 (1927); **32**, 961 (1928).

[3] G. N. Glasoe, Phys. Rev. **38**, 1490 (1931).

same thing is true of nickel. As more data are obtained it may be expected that we will find a still more definite relation between photoelectric threshold and atomic number and this should be of considerable assistance in formulating our theories of surface work functions.

Although the present study was undertaken merely for the purpose of determining the photoelectric and thermionic work functions of palladium, while the work was in progress an important paper was published by R. H. Fowler[4] in which he proposed a new theory of photoelectric emission. It seemed highly desirable, therefore, to obtain the additional data required to put the theory to an experimental test. This was done and the results, as will be seen, furnish a valuable quantitative verification of the theory.

II. Apparatus and Methods

Tube and vacuum system

The experimental tube was very similar to that used by DuBridge[2] in his study of platinum. It consisted of a Pyrex tube, with a strip of Pd foil suspended along the axis of three coaxial nickel cylinders, the two outer ones acting as guard rings and being connected to ground. The central collecting cylinder was connected to the electrometer through a well insulated seal at the side of the tube. A quartz window, attached by means of a graded quartz-to-Pyrex seal just opposite a circular opening in the collecting cylinder, served to admit the light when photoelectric readings were being taken, and to allow focussing of the optical pyrometer during temperature measurements. A magnetically operated shutter protected the window from deposits of vaporized palladium during the long outgassing process.

The vacuum system consisted of an air-cooled mercury diffusion pump in series with a Cenco-Hyvac pump, these being separated from the experimental tube by means of a mercury cut-off and liquid air trap. The system contained no waxed seals and all stopcocks were restricted to the low-vacuum side. Pressures below the range of the McLeod gauge were measured by an ionization gauge, and were below 10^{-7} mm Hg in the final stages.

Filament outgassing

After a thorough cleaning of the tube and foil, the tube was sealed to the pumps and baked at temperatures as high as 485°C for from 20 to 30 hours, the filament being kept at a dull red heat by means of an electric current from a low voltage transformer. All metal parts were thoroughly outgassed by means of a high frequency induction furnace. During the initial outgassing the liquid air level was kept fairly low to condense vapors in the bottom of the trap, and was later raised to prevent their escape into the system.

The specimen to be examined consisted of a ribbon of very pure palladium $120\times4.5\times0.01$ mm, bent in the form of a loop and suspended inside the collecting cylinders by means of heavy tungsten leads. There was great difficulty in getting the filament to survive the complete outgassing treatment. Most of the specimens developed hot spots after 75 to 300 hours of treatment at

[4] R. H. Fowler, Phys. Rev. **38**, 45 (1931).

1300°K and broke at these points, although this temperature is several hundred degrees below the melting point of palladium. The broken filaments showed a very marked crystallization near the break and under the microscope had an appearance very similar to micro-photographs of aged palladium foils published by Utterback.[5] The breaks seemed to occur along the crystal boundaries. This early failure of the filaments was finally overcome by beginning the outgassing process at much lower temperatures (<900°K), and, after 500 or 600 hours of heating, raising the temperature slowly to 1300°K with an occasional flashing at 1400°K. This greatly reduced the rate of evaporation and of crystallization and allowed the specimens to survive for 1000 hours or more, during which time the photoelectric behavior reached a steady state which could not be changed by further treatment. During most of the heating the filament was maintained 200 volts positive with respect to the cylinders, to assist the positive-ion emission (presumably gas ions) from the filament. The positive-ion currents were very large at first but decreased rapidly during outgassing, although they never completely disappeared.

Photocurrents were measured by means of a Compton electrometer whose sensitivity was varied from 5000 to 16,000 mm per volt depending on the emission to be measured. The rate-of-charge method was used. For thermionic currents, the electrometer was shunted to ground through one of several high resistances (10^7 to 10^9 ohms) and through a resistance-box potentiometer. It thus became a steady-deflection instrument, a null method of measurement being used. Dr. L. C. Van Atta of this laboratory made the high resistances used.[6]

In order to obtain steady heating currents while runs were being taken, a 24-volt bank of large storage cells was connected in series with a set of fixed wire resistances of negligible temperature coefficient. In this manner heating currents could be kept constant to about 0.001 amp.

Temperature measurements

At incandescent heat the temperature of the palladium was measured with a disappearing-filament type of optical pyrometer, which had previously been calibrated against a standard tungsten lamp supplied to this department by Dr. Forsythe of the Nela Park Laboratories. The true temperature was obtained from the brightness temperature using published tables for platinum,[7] the emissivities of palladium and platinum being the same. The lower temperatures were determined by measuring the resistance of the filament.

Source of light

The source of illumination was a vertical air-cooled quartz mercury arc operated at 90 volts and 2.0 amperes. The light was resolved by a Hilger,

[5] C. L. Utterback, Rev. Sci. Inst. **1**, 39 (1930).

[6] The method of making these resistances has been described in Rev. Sci. Inst. **1**, 687 (1930).

[7] International Critical Tables, Vol. V, p. 245.

quartz-prism, constant-deviation, monochromatic illuminator and focussed on the filament by a quartz lens. Relative intensities of the spectral lines were obtained from the response of a quartz sodium photoelectric cell connected to a direct-current amplifier, the cell having been previously calibrated by means of a tungsten lamp. This method will be described in detail elsewhere.

III. Photoelectric Results

The general trend of the photoelectric threshold during outgassing is shown in Fig. 1, in which the longest wave-length at which an emission was detected at room temperature is plotted as a function of the degassing time. The general shape of this curve is characteristic of all specimens examined. In all cases thresholds below 2300A were observed for fresh specimens. The

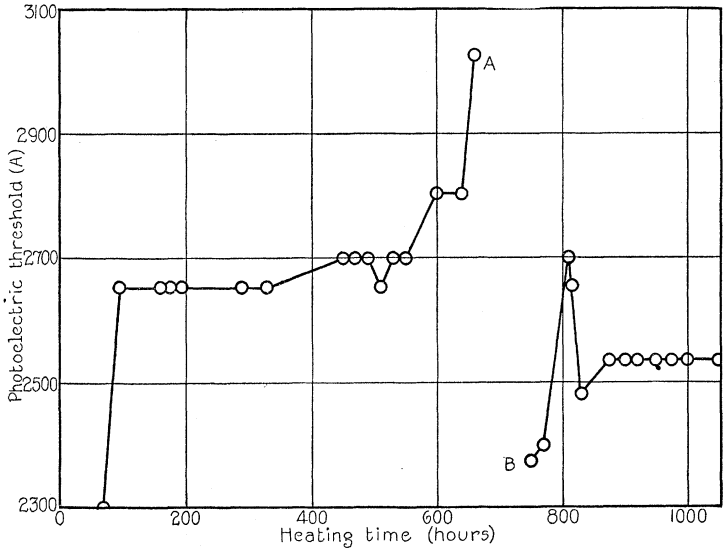

Fig. 1. Behavior of the photoelectric threshold for Pd during outgassing. The discontinuity AB was caused by rebaking the tube.

speed with which the long wave limit increased during the initial stages depended very greatly on the outgassing temperature. For example, for the specimen represented in Fig. 1 the threshold did not reach its maximum value (3022A) until after 600 hours of treatment at 900°K, while for other specimens a threshold of approximately 3300A was reached after only 25 hours at 1400°K. The severe initial treatment resorted to in the latter case, although it seemed to speed up the process, so weakened the specimen by evaporation and crystallization that it invariably failed to withstand further treatment long enough to reach a final stage. In Fig. 1 the sudden drop in threshold value from A to B at 660 hours is the result of rebaking the experimental tube. Exposing the filament to air for a short time at a pressure of several cm Hg resulted in the temporary increase in λ_0 shown at 800 hours. The long wave-length limit then decreased to 2536A at room temperature and

did not change for the last 200 hours. A hot spot which developed during the last 100 hours made further treatment at higher temperatures impossible. The final value of the surface work function for this specimen was 4.95 volts as calculated from extrapolation of $f(\lambda)$ curves for room temperature and 4.93 volts when the Fowler method of plotting was used. More reliable readings were obtained from another specimen which had been treated in a manner similar to that described above but which withstood over 1000 hours of outgassing treatment. The final value of the threshold for this specimen, obtained from the $f(\lambda)$ curve for room temperature (shown in Fig. 3 below), was

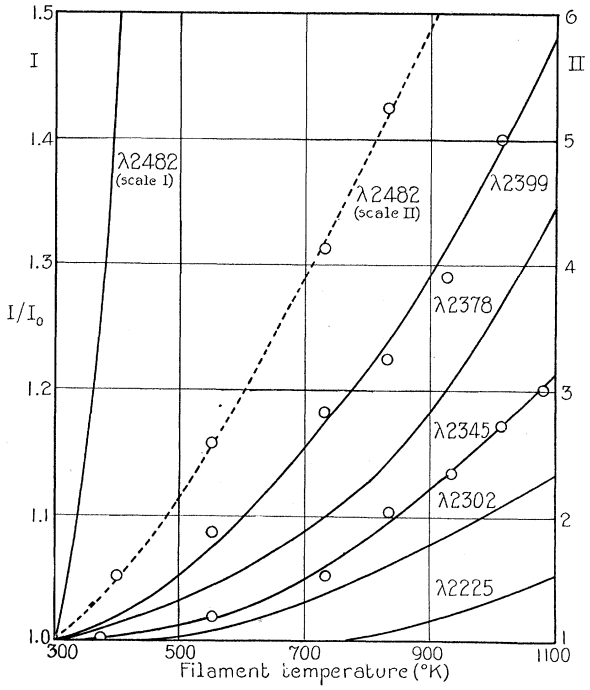

Fig. 2. Temperature variation of photo-currents.

2486A (4.97 volts). When the Fowler method of analysis was employed (see Fig. 4) the same value of the work function was obtained, and this may therefore be taken as the best value for the photoelectric work function of thoroughly outgassed palladium.

IV. Temperature Variation[8]

The variation with temperature of the photoelectric current from clean Pd excited by light is shown in Fig. 2, in which the ratio (I/I_0) of the photocurrent at a given temperature T to that at room temperature is plotted as a function of T. When the specimen had reached its steady state these curves were completely reproducible. It is seen that for wave-lengths far from the

[8] This problem is further discussed in the next paper in this issue of the Physical Review.

threshold (λ2225) the effect of temperature is almost negligible, while near the threshold (e.g., λ2482) the current increases very rapidly with temperature. (The curve for λ2482 is represented by the dotted line when the vertical scale is contracted ten-fold.)

The ordinary spectral distribution curves for three temperatures are shown in Fig. 3. The pronounced feet of these curves, especially at higher temperatures, are not due to scattered light. The curves do not cut the axis at any definite wave-length, but approach it asymptotically, the approach being more gradual for the higher temperatures. All of these curves are quite similar to those obtained by Winch,[9] Morris,[10] and Cardwell[11] for Ag, Au, and Ta surfaces respectively. It is seen from Fig. 3 that in the temperature range

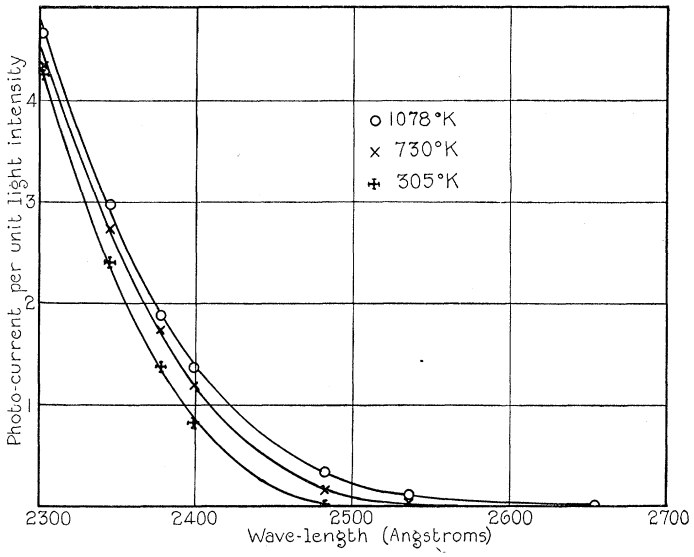

Fig. 3. Spectral distribution curves for outgassed Pd.

used, 305° to 1078°K, the threshold seemed to shift from about 2490A to 2660A corresponding to a change in work function from 4.95 to 4.64 volts. If, however, the approach is asymptotic, as predicted by R. H. Fowler,[4] and as indicated by Fig. 3, then the longest wave-length at which an effect is observed is limited only by the sensitivity of the measuring instruments used.[12] Thus the so-called "shift" in threshold has lost its meaning. Fowler has

[9] R. P. Winch, Phys. Rev. **37,** 1269 (1931).

[10] L. W. Morris, Phys. Rev. **37,** 1263 (1931).

[11] A. B. Cardwell, unpublished data quoted by R. H. Fowler (reference 4).

[12] The asymptotic approach of these curves to the axis is due to the thermal energies of the electrons. Suhrmann (Zeits. f. Physik **33,** 63 (1925)) pointed out that, on the basis of the *classical* electron theory of metals, the curves should be of this form, and he found this to be the case experimentally. Lawrence and Linford (Phys. Rev. **36,** 482 (1930)) obtained similar curves for K layers on W and stated that they could be accounted for by thermal energies of the electrons as given by the Fermi-Dirac statistics. The first quantitative treatment of this problem is that given by Fowler.

pointed out that the method of extrapolating the $f(\lambda)$ curves to zero current, hitherto employed to obtain the threshold, is no longer valid, and he has given a new method for evaluating this constant. It will be shown in the following section that Fowler's theory completely accounts for the temperature variation represented in Figs. 2 and 3.

V. Comparison with Fowler's Theory[8]

Fowler's theory leads to the result that the photoelectric current I excited in a metal surface at the temperature T by unit intensity of light of frequency ν is given by the relation

$$\log I/T^2 = \Phi(\mu) + \text{const.}$$

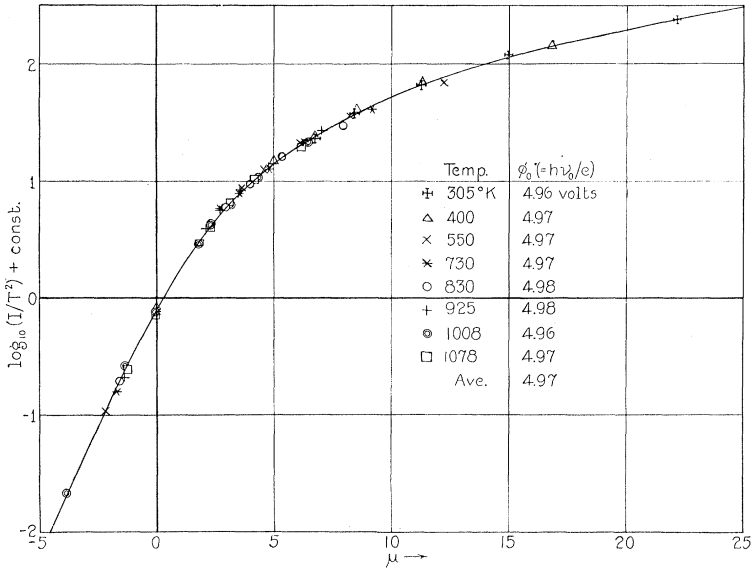

Fig. 4. Analysis of photoelectric observations by Fowler's method.

where $\mu = h(\nu - \nu_0)/kT$ and $\Phi(\mu)$ is a universal function of μ. ν_0 is the threshold at 0°K. If $\Phi(\mu)$ is plotted against μ the curve shown in Fig. 4 is obtained. To obtain ν_0 for a given surface the photoelectric observations at a given temperature are plotted in the form log I/T^2 against $h\nu/kT$, and the horizontal component of the shift required to make this curve fit the theoretical curve is equal to $h\nu_0/kT$. Fowler showed that his theory was in good agreement with the results of Winch,[9] Morris,[10] and Cardwell,[11] but it is highly desirable to make further experimental tests.

An analysis by Fowler's method of the data for clean Pd is also shown in Fig. 4, in which the experimental points are plotted after they have been shifted by the proper amounts. Observations of I as a function of ν were taken for 8 different temperatures in the range 305°K to 1078°K, yielding 8 observed curves. The *vertical* shifts required to bring these curves into coincidence with the theoretical curve were the same for all temperatures, as de-

manded by Fowler's theory. From the *horizontal* shifts the work functions shown in the figure were computed. The individual values show an excellent agreement among themselves, yielding an average value of 4.97 ± 0.01 volts (2486A). This happens to be in good agreement with the value obtained by extrapolating the $f(\lambda)$ curve taken at room temperature (Fig. 3). Fowler's method, however, gives the *true* or absolute zero value of the work function which is not affected by an arbitrary extrapolation of a curve which really approaches the axis asymptotically.

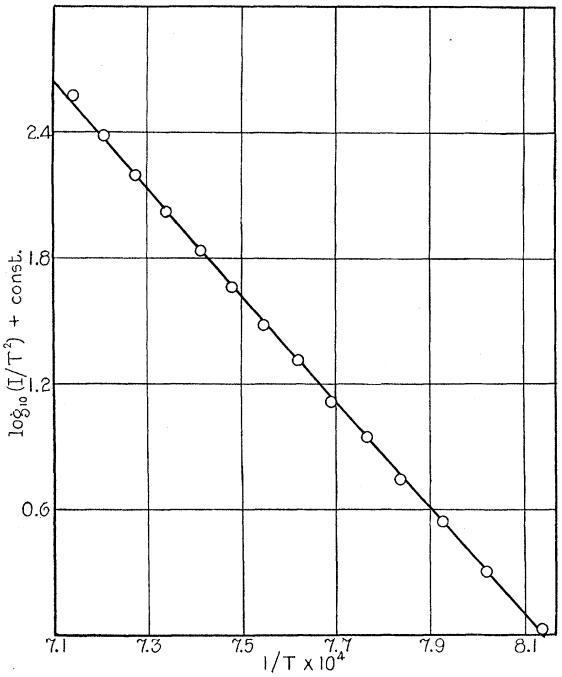

Fig. 5. Thermionic curve for outgassed Pd.

Application of Fowler's method to observations made before the specimen had reached a final state also gave a good fit, as well as good agreement in the values of ϕ_0 for various temperatures. It is to be concluded, therefore, that Fowler's theory is applicable not only to surfaces entirely free from gases but also to all surfaces in a state sufficiently stable to prevent any appreciable change during the course of the observations.

VI. Thermionic Measurements

In taking thermionic measurements, simultaneous readings were taken of the thermionic current and filament temperature. The true temperature, as determined from the average of several pyrometer settings, was plotted as a function of the filament heating current and the final temperatures were read from a smooth curve drawn through the experimental points.

After repeated attempts it was found that no systematic study of the behavior of the thermionic work function during the outgassing process could be made, since the temperatures required for thermionic measurements were higher than the temperatures at which the filament could be heated safely during the initial stages. It was found, however, that the thermionic work function decreased from high initial values down to values as low as 2.0 volts, and this was followed by a subsequent rise, in line with the corresponding photoelectric changes. Satisfactory thermionic measurements after the final state was reached were obtained for only a single specimen (the one for which the curves of Figs. 2, 3, and 4 are plotted), and this specimen developed a hot spot and burned out before the run could be repeated. The data for this run are shown in Fig. 5, plotted in the usual form for determining the work function in Richardson's equation,

$$I = AT^2e^{-b/T}.$$

The value of b is 57,950°K corresponding to a work function of 4.99 volts, with a possible error of about 1 percent.

Fowler's theory predicts that the value of the thermionic work function should be equal to the *true* photoelectric work function ϕ_0, determined by the method outlined in the previous section. It is seen that this prediction is verified within the limits of experimental error, the values being 4.99 ± 0.04 volts and 4.97 ± 0.01 volts, respectively. This point is of interest since it has not been previously tested directly and since it has occasionally been suggested that the thermionic and photoelectric work functions, in order to agree, should be measured at the *same* temperature. In the present experiments, however, if the photoelectric threshold is determined at high temperatures by the usual extrapolation methods, a work function is obtained (4.64 volts) which differs by 7 percent from the thermionic value. This furnishes further striking evidence in favor of Fowler's theory.

The average value of the thermionic coefficient A, although it could not be determined with high accuracy in these experiments, came out very close to the theoretical value of 60 amp/deg^2. cm^2, with a maximum deviation of about 30 percent from this value. This is in interesting contrast to the results for Pt which yielded very high values of A, although the two metals, since they occupy similar positions in the periodic table, would be expected to show a similar thermionic behavior. However, this result confirms the suggestion[13] that high values of A occur only with unusually high values of b.

The experimental work described in the present paper was assisted by a grant to the senior author from the Science Research Fund of Washington University.

[13] L. A. DuBridge, Proc. Nat. Acad. Sci. 14, **78** (1928).